THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS CONTAINING ASYMMETRIC COMPONENTS

BY

OREN FRANCIS WILLIAMS

B.Eng., University of Toledo, 1943
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

The possibilities of resolution of racemates on the basis of preferential coordination of one of the optical antipodes of a racemic mixture to the exclusion of the other has been demonstrated by the work of Jonassen (1), Hamilton (2), Johnson (3), and Sister Mary Martinette (4).

Jonassen was able to effect a partial resolution of racemic tartaric acid into its optical antipodes on the basis of his experimental observation that of the two tartrato complexes, [Co *l*-pn_2 *d*-tart]Cl and [Co *l*-pn_2 *l*-tart]Cl, the *levo*-tartrato complex reacted many times more rapidly than the *dextro*-tartrato complex with *levo*-propylenediamine to yield the *tris-levo*-propylenediamine cobalt(III) ion. Subsequent work by Hamilton further substantiated the validity of Jonassen's approach by demonstrating experimentally that *dextro*-tartaric acid replaced the coordinated tartrato group in the complex, [Co *l*-pn_2 *l*-tart]Cl. Johnson, in a modification of Jonassen's procedure but employing the same general principle of coordinative selectivity of optical antipodes, effected an almost 70 percent resolution of propylenediamine.

Theoretical And Discussion Of Results

The present investigation was initiated with the purpose of studying further the phenomena of preferential coordination observed with the cobalt complexes of propylenediamine. At the outset it was considered a good possibility that an introduction of more asymmetry into the coordination sphere might reenforce the selectivity of the coordination sphere toward the entrance of optical isomers. To increase the asymmetry within the coordination sphere above and beyond that existing in

the cobalt(III) complexes of *levo*-propylenediamine required a cobalt amine complex containing an organic diamine with two asymmetric centers instead of one. The particular amine chosen for this work was 1,2-diphenylethylenediamine which contains two similar asymmetric carbon atoms and is therefore capable of existing in both a racemic form and a *meso*- form.

Since neither the racemic form nor the *meso*- form of 1,2-diphenylethylenediamine are commercially available, it was necessary to find a convenient method for their synthesis. Of the several different methods reported in the literature, the one reported by Lifschitz (5) appeared to be most promising. It was found, however, that several modifications of Lifschitz's procedure were necessary to prepare the amine in good yield by a convenient procedure. Several modifications of Lifschitz's procedure were made and in general the procedure was improved to the extent that the amine can now be prepared in the laboratory on a relatively large scale and in good yields. The synthesis as modified involves the condensation of benzaldehyde with liquid ammonia to yield hydrobenzamide which is subsequently rearranged to isoamarine by heating at 120°C. The amarine so produced is in turn rearranged to isoamarine by heating at 160°C in a diethyleneglycol solution containing sodium hydroxide. Isoamarine is acetylated and the acetyl derivative is subsequently hydrolyzed to yield racemic-N-acetyl-N′-benzoyl-1,2-diphenylethylenediamine. Hydrolysis of the diacyl derivative with a mixture of glacial acetic acid and hydrobromic acid yields the amine dihydrobromide from which the free amine is obtained by treatment with a solution of sodium hydroxide. The *meso*- form of the amine is obtained in a similar manner except that amarine is acetylated and subsequently hydrolyzed to the amine.

In contrast to the cobalt complexes of propylenediamine and ethylenediamine, the cobalt complexes of 1,2-diphenylethylenediamine are in general soluble in polar organic solvents but insoluble in water. Evidence obtained indicates that the complexes containing the *meso*- amine are much less stable and more difficult to prepare than complexes containing

the racemic or active amine.

Trans-dichloro-*bis*-1,2-diphenylethylenediamine cobalt(III) complexes containing the racemic, *meso*-, or *levo*- form of the amine were prepared by hydrogen peroxide oxidation of a mixture of the amine and cobalt(II) chloride dissolved in ethanol. The *trans*-dichloro complex containing the racemic form of the amine was found to be extremely stable toward thermal decomposition as well as toward rearrangement to the *cis*-dichloro isomer. Attempts to rearrange the *trans*- complex to the *cis*- isomer by the methods applicable to the corresponding propylenediamine and ethylenediamine complexes were unsuccessful. The *cis*-dichloro complex was obtained, however, by treatment of carbonato *bis*-racemic-1,2-diphenylethylenediamine cobalt(III) nitrate with gaseous hydrogen chloride. The *cis*-dichloro complex rearranged rapidly to the *trans*-isomer when dissolved in ethanol or heated in an oven at 90°C. An attempt to obtain additional proof of the *cis*- configuration of the complex by comparison of its X-ray diffraction pattern with that of the *trans*- isomer was unsuccessful since the *cis*-dichloro complex was found to be amorphous.

The method found to be most convenient for the preparation of the carbonato complexes containing 1,2-diphenylethylenediamine involved the displacement of ammonia in carbonato tetrammine cobalt(III) nitrate by refluxing the carbonato complex with an alcohol solution of the amine. The reaction was found to yield two different carbonato complexes, one containing two molecules of water, $[Co(stien)_2CO_3]NO_3 \cdot 2H_2O$, and the other containing one molecule of water, $[Co(stien)_2CO_3]NO_3 \cdot H_2O$. The two products differed markedly in physical and chemical characteristics. The chemical behavior of the dihydrate indicated that the carbonate ion was unidentate whereas the carbonato group in the monohydrate appeared to behave as a bidentate ligand. Absorption spectra data could not be obtained for the dihydrate due to its extreme insolubility in all solvents. The absorption peaks of the monohydrate appeared at about the same wave lengths as those reported for the corresponding propylene-

diamine complex.

The tartrato complexes of racemic and *levo*-1,2-diphenylethylenediamine were prepared by the reaction of silver tartrate with *trans*-dichloro-*bis*-1,2-diphenylethylenediamine cobalt (III) nitrate. All of the tartrato complexes prepared and dried at room temperature had the composition calculated for the dihydrate. Drying at elevated temperatures *in vacuuo* failed to remove all of the water which analysis indicated to be present. Attempts to obtain a resolution of racemic tartaric acid by preferential coordination were unsuccessful. The tartrato complexes, when dissolved in ethanol, reacted slowly when boiled with barium chloride to precipitate barium tartrate. In general the behavior of the tartrato complexes seemed to indicate that the tartrato ligand was very firmly bound to the coordination sphere. Unlike the other complexes of racemic and *meso*- 1,2-diphenylethylenediamine, the tartrato complexes could not be obtained in crystalline form from their concentrated alcoholic solutions. The general behavior of the tartrato complexes suggests the possibility that the tartrate group may behave as a unidentate group with a water molecule occupying the other *trans*- position. In view of the very unsymmetrical arrangement of the groups in the coordination sphere which would be necessitated by the tartrato group behaving as a bidentate group along with the already observed instability of the *cis*-type configuration, it appears likely that if the tartrato group is bidentate in these complexes the bonding is weak. If such is the case, the rearrangement of the bidentate group with a molecule of water occupying the sixth position *trans*- to it might be expected. With the tartrate group behaving as a unidentate group the degree of preferential coordination would be expected to be much less than that observed for the corresponding tartrato complexes containing *levo*-propylenediamine.

The dinitro, *bis*-sulfito, *bis*-thiocyanato, and oxalato cobalt(III) complexes containing 1,2-diphenylethylenediamine were prepared by substitution reactions similar to those employed for the synthesis of the corresponding propylene-

diamine and ethylenediamine complexes. Their general chemical characteristics as well as the absorption spectra of their alcohol solutions were found to be very similar to the analogous propylenediamine and ethylenediamine complexes.

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VITA

The author was born in Oakland City, Indiana, on March 5, 1920. He received his elementary and secondary education in the public schools of that city, graduating from Oakland City High School in May 1938. His undergraduate training was received at the University of Toledo where he was awarded the degree of Bachelor of Engineering in September 1943. In the same month he entered the United States Navy and was discharged in November 1944. He accepted a position in the same year with the Illinois State Geological Survey where he worked as a research chemist until September 1947. During his employment with the Illinois State Geological Survey he attended the Graduate College of the University of Illinois part time. The degree of Master of Science in Chemistry was received in June 1947. In September 1947 he accepted a teaching assistantship in the Inorganic Division and continued his graduate studies.

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